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(54) COOLING TUBULAR EXTRUDATES

(71) We IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the production of tubular extrudates, and, in particular, to a method for cooling an extruded tube of plastics material.

Oriented tubular film is usually produced by extruding a relatively thick-walled thermoplastics tube from an annular orifice, and subsequently stretching the extruded tube, at a temperature above the glass transition temperature (Tg) and below the melting temperature of the thermoplastics material, in the transverse and/or longitudinal directions to form a thin film, the stretching being effected in the transverse direction by means of internal gas pressure and in the longitudinal direction by withdrawing the tube at an accelerated rate in the direction of extrusion. In the case of oriented films produced from crystallisable polyesters, the polyester should be in a substantially amorphous state when stretched, and the extrudate must therefore be rapidly cooled, prior to reheating and stretching, to retain the polymer in the amorphous state. Likewise, in the formation of oriented films from crystalline polymers, such as polyolefines, it is necessary to cool the extrudate to produce sufficient nuclei to ensure that individual spherulites remain small, thereby enabling the extruded tube to be readily stretched, when reheated, to yield a transparent film.

Cooling of the extruded tube is conveniently effected internally and/or externally. For example, the tube may be internally cooled by means of a cooling mandrel located within the tube in the vicinity of the die from which the tube is extruded, while external cooling may be effected by passing the tube through a closely-fitting cooled sleeve. Efficient transfer of heat from the tube to the mandrel- or sleeve-cooling surface may be ensured by flowing a lubricating heat-transfer liquid between the tube and that surface. By simultaneously cooling the exterior and interior surfaces of the extruded tube, increased rates of tube production may be achieved.

Difficulty has been experienced, particularly at high extrusion rates, in producing a cooled, or cast, tube of uniform dimensions. In particular, as the extrusion rate increases, cast tube formed using an internal mandrel cooling system frequently exhibits a profile defect manifesting itself as a generally helical ridge running along and around the tube surface. Although cast tube exhibiting this so-called "helix" defect can be converted to tubular film, the latter is characterised by a non-uniform profile and also exhibits haze bands which render the film unsuitable for commercial exploitation. A similar problem is encountered in the production of relatively thick film.

Proposals which have been made to reduce the incidence of "helix" include: increasing the rate of flow of heat-transfer liquid; altering the separation between the cast tube and cooling surface; and, employing an internal mandrel having profiled fins on the surface thereof. However, a tubular film-forming process is sensitive to minor variations in operating parameters, and it is frequently observed that adoption of one or more of the aforementioned proposals introduces a further undesirable characteristic in the resultant film. Occasional adjustment of an operating parameter in an attempt to eliminate the intermittently occurring "helix" defect is, therefore, undesirable.

We have now devised an improved technique for cooling an extruded tube.

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Accordingly, the present invention provides a method of cooling an extruded tube of plastics material comprising feeding the tube, in the direction of extrusion, in heat-transfer relationship with an adjacent cooling surface, maintaining said cooling surface at a temperature below the melting point of the plastics material, maintaining between, and in contact with, the tube and said cooling surface, a continuous sheath of a heat-transfer liquid having a dynamic viscosity at 20°C of from 2 to 20,000 centipoise, and withdrawing the cooled tube from said surface.

The heat-transfer liquid should be "inert", to the extent that it does not react with the tube-forming material during the cooling operation to impair the desired characteristics of the tube, and, in particular, does not detract from the physical and optical characteristics, such as haze and gloss, of film subsequently formed from the cooled tube. Additionally, the liquid should exhibit good thermal conductivity, and, preferably, should be an acceptable contaminant for materials, such as foodstuffs, which will subsequently be in contact with the cooled tube, or packaged in a film derived therefrom. Water, having a dynamic viscosity at 20°C of approximately 1 centipoise (cP), is usually employed as a heat-transfer liquid (coolant) in conventional film-forming operations, and in the process of the present invention an aqueous medium of the required viscosity is preferably employed. Other suitably inert and viscous heat-transfer liquids may, of course, be employed, if desired.

The selected viscosity of the heat-transfer liquid should be such as will permit adequate heat-transfer between the tube and adjacent cooling surface without significantly impeding movement of the tube relative to that surface. In practice, the required viscosity is readily established by simple experimentation, and conveniently is within a range of from 5 to 20,000 cP, although the upper viscosity limit should be selected so that the flow of the viscous liquid through the associated pumping equipment and plumbing is not unduly impeded. To ensure the absence of "helix" despite normal fluctuation in plant parameters, the viscosity is preferably maintained at not less than 10 cP, and preferably from 10 to 10,000 cP. A particularly preferred viscosity range is from 25 to 1000 cP.

Where the selected heat-transfer liquid does not inherently possess the required dynamic viscosity characteristics, conventional viscosity modifiers, including cellulosic derivatives, and soluble starches and starch ethers, may be employed to adjust the viscosity of the liquid to the desired level, provided that the modifier is such as will not impair the desired characteristics of the cooled tube - or of film formed therefrom. Thus, water may be thickened to the required viscosity by addition of the appropriate amount, usually of the order of from 0.25 to 5% by weight of the solution, of a cellulosic resin, for example - an alkyl cellulose or a sodium carboxymethyl cellulose of the kind commercially available as a domestic wallpaper paste, or by the addition of a water-soluble polymeric resin, such as the polyethylene oxide resins supplied by Union Carbide Corporation under the trade name POLYOX (Registered Trade Mark). An aqueous solution or dispersion of the appropriate viscosity is therefore readily prepared, and is particularly suitable for use as a heat-transfer liquid in the process of the present invention.

Viscosity values referred to herein are determined at 20°C using a Brookfield Viscometer, type LVF, with a No. 1 spindle rotating at 30 revolutions per minute (rpm).

According to one embodiment of the invention the cooling surface is in the form of a cooled, preferably tapered, internal mandrel, coaxial with, and of diameter not exceeding that of, the extrusion orifice, and located within the extruded tube.

A typical lubricated mandrel system suitable for the production of polyolefine films, to which the techniques of the present invention may be applied, is described in British Patent No. 1 284 321 which relates to the cooling of an extruded tube by passing a tube of a thermally softened polymeric material, extruded from a die, over an internal cooling mandrel, continuously supplying a sheath of heat-transfer liquid to between the mandrel and the tube, maintaining, at the end of the mandrel remote from the extruder, a head of liquid capable of exerting pressure on the sheath of liquid, and withdrawing the liquid from the head, wherein the pressure of the liquid between the mandrel and the tube at any one point is greater than the pressure on the outside of the tube at that point. Extrusion of the tube is preferably effected in a substantially vertically downwards direction, and the sheath of heat-transfer liquid is conveniently supplied by overflow from a circumferential channel at the upstream end of the mandrel, i.e. adjacent the extrusion die. The space between the die and upstream end of the mandrel therefore need not be, and preferably is not, completely filled with heat-transfer liquid. Consequently the liquid does not make contact with the hot die, and therefore is conveniently selected from that group of liquids having a boiling point less than the temperature of the die; otherwise, if the aforementioned space is completely filled with liquid, the latter must be selected from the relatively restricted group of liquids having a boiling point greater than the die temperature so that boiling of the liquid, which mars the tube surface, does not occur adjacent the die.

According to a further embodiment of the invention the cooling surface is in the form of a

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cooled annular passageway into and through which the extruded tube is passed. A typical system of this kind, the so-called "weir" system, is described in British Patent No. 741 963 which relates to the production of thin-walled tubing or tubular film by continuously extruding a molten organic thermoplastics material in tubular form, and continuously withdrawing the tubing downwardly in a substantially vertical direction from the extruder while maintaining within the tubing a volume of gas such that the degree of inflation and the rate of withdrawing the tubing bring about a reduction in thickness of the tubing, wherein the inflated tubing is passed through a passageway which, at least at the entrance end for the tubing, is of substantially circular cross-section, and which is interiorly bathed by a downwardly flowing heat-transfer liquid which contacts the whole of the external surface of the tubing or tubular film as it passes through the passageway.

Although an internal mandrel will not normally be employed in combination with a closely-fitting external lubricated sleeve of the kind disclosed in British Patent No. 741 963, a mandrel may conveniently be employed in combination with an external liquid cooling bath of larger internal diameter, as disclosed in British Patent No. 1 284 321.

In addition to its cooling function, the cooling surface also serves to size or dimension the extruded tube, and it is therefore desirable that the sheath of heat-transfer liquid should be as thin as practicable, so that the tube conforms closely to the shape of the cooling surface. In the case of an internal mandrel cooling surface, the thickness of the heat-transfer liquid sheath is conveniently from 200 to 500 microns, while with an external cylindrical "weir" cooling surface a sheath thickness of from about 200 to 1300 microns is suitably employed.

The rate at which the heat-transfer liquid should be supplied to maintain a continuous sheath of appropriate thickness between the tube and cooling surface is readily determined by simple experimentation. In practice, to eliminate the "helix" defect we prefer that the heat-transfer liquid should be supplied at a rate of at least 0.02 litres/minute/centimetre peripheral width of tube surface (i.e. the width measured around the periphery of the tube in a plane substantially normal to the longitudinal axis thereof), conveniently between 0.02 and 0.5, and preferably between 0.05 and 0.15 litres/minute/centimetre width.

Continuity of the liquid sheath is also encouraged by pressurising the sheath, suitably by association with a suitable head of liquid as hereinbefore described, so that the pressure exerted by the heat-transfer liquid between the cooling surface and tube at a selected point exceeds the pressure on the opposite surface of the tube wall at that point.

In the case of an internal mandrel system using water as a heat-transfer medium between the mandrel and tube, an experimental investigation involving the injection of dye into the water at the upstream end of the mandrel has established that the "helix" deformity is apparently associated with a variation in the thickness of the water sheath along the length of the mandrel, and is particularly prevalent in the presence of unstable flow conditions such that tongues of water are forced spirally around the mandrel surface rather than forming a uniform, constant thickness, axially-flowing sheath along the length of the mandrel. Progressively increasing the viscosity of the water by the introduction of a thickening agent, such as a water-soluble polyethylene oxide resin, apparently assists the formation of a continuous and uniform sheath, and results in a progressive reduction, and eventual elimination, of the "helix" defect.

The process of the present invention is therefore particularly advantageous in that it enables tubular film of uniform dimensions and good optical characteristics to be produced. Furthermore, the rate of film production may be increased, and thicker films may be produced without increasing the incidence of profile defects which occur when water *per se* is employed as a heat-transfer medium.

Although the process of the present invention may be employed to cool tubes derived from any extrudable materials, the process is preferably employed in relation to the production of tubular films from any thermoplastics polymeric material, and particularly in the production of films and tubes from crystalline or crystallisable polymers. For example, polymers and copolymers of 1-olefines, such as high density polyethylene, polypropylene or ethylene propylene copolymers, of polybutene-1, of poly-4-methyl pentene-1, of polyesters such as polyethylene terephthalate and polyethylene-1,2-di-phenoxyethane-4,4′-dicarboxylate, of polysulphones, and of the various nylons, may be processed. A suitable film-forming material is a high molecular weight stereoregular predominantly crystalline polymer of propylene, either in the form of a homopolymer or copolymerised with minor quantities (e.g. up to 15% by weight of the copolymer) of other unsaturated monomers, such as ethylene. Coated films and coextruded multiple-layer films may also be processed.

An oriented tubular film is suitably produced by melt extruding the desired polymeric material in tubular form from a simple annular die, cooling the extruded tube by the process of the present invention, reheating and inflating the tube by the so-called "bubble" process to introduce transverse orientation, and simultaneously elongating the tube longitudinally to orient the film in a lengthwise direction. The film is then preferably "heat-set", i.e.

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dimensional stability of the film is improved by heating the film, while restrained against thermal shrinkage, to a temperature above the glass transition temperature of the polymer from which the film is formed but below the melting point thereof.

A similar technique employing a multi-channel, annular, coextrusion die is suitable for the production of multiple-layer films, such as a polypropylene substrate having on at least one surface thereof a layer of a copolymer of propylene (80 to 95% by weight) with another alphaolefine containing from 4 to 10 carbon atoms, such as butene-1.

Films made from tubes cooled according to the present invention may conveniently contain any of the additives conventionally employed in the manufacture of thermoplastics films. Thus, additives such as dyes, pigments, lubricants, anti-static agents, anti-oxidants, anti-blocking agents, surface-active agents, slip aids, stiffening aids, gloss-improvers, prodegradants, and ultra-violet light stabilisers may be employed.

The films may be subjected to conventional after-treatments - for example, exposure to a corona discharge treatment to improve the bonding and print-receptive characteristics of the film surface, and may vary in thickness depending on the intended application. Films having a thickness of from 2 to 150 microns are of general utility, while those intended for use in packaging operations are suitably within a thickness range from 10 to 50 microns.

The invention is illustrated by reference to the drawing accompanying the provisional specification in which:

the single Figure is a simplified schematic elevation, not to scale, depicting the production of an oriented tubular film from a cast polymeric tube extruded onto a lubricated internal mandrel cooling surface.

Referring to the drawing, a tube of thermoplastics material 1 is extruded from an annular extrusion die 2, and withdrawn therefrom by a pair of contra-rotating nip rolls 3 which are of width less than the collapsed tube, and therefore do not collapse the tube across its entire width. The rolls 3 withdraw the tube at a rate greater than that at which it is extruded, thus hauling the tube down on to a tapered cooling mandrel 4 situated inside the tube, and forwarding the cooled tube for further treatment. An aqueous heat-transfer medium is supplied through pipe 5 to an annular channel 6 at the upstream end of the mandrel where it is allowed to accummulate as a small pool or head of liquid in the space 7. The aqueous medium is therefore carried down from space 7 as an annular sheath 8 between the mandrel 4 and the tube 1 into the chamber 9 formed between the bottom of the mandrel and a resilient sealing member 10, and enters a pipe 11 which is normally open to atmosphere. Within pipe 11 is located an axially-slideable dip pipe 12 through which the aqueous medium is removed by the application of suction, the downstream end of pipe 12 being located so as to create a head of liquid in pipe 11 which exerts pressure on the liquid in chamber 9 and thence on the liquid sheath 8. Liquid removed via pipe 12 may be discarded, or, if desired, returned to a reservoir (not shown) from which it can be recirculated to inlet pipe 5 after appropriate adjustment of its temperature and viscosity.

Below sealing member 10 is positioned a circular sponge 13 which contacts the inside of the tube 1 to remove any of the liquid medium which passes the seal. This moisture is removed from the sponge 13 by applying suction to a pipe (not shown) passing through the interior of the mandrel.

In practice an intermediate sealing member is usually positioned between sealing member 10 and sponge 13, together with means to pressurise the tube in this region, but these details are omitted for clarity, as are details of the system for circulating a liquid coolant through the interior of the mandrel.

As well as being cooled internally by the mandrel, the tube 1 is cooled externally by passage through a water bath 14 which surrounds the tube. Water is continually introduced into the external bath through pipe 15, and flows in an upstream direction over annular baffle 16 and out through pipe 17. After passing through the water bath, the cooled tube passes through a chamber 18 in sealing engagement with the tube by virtue of flexible annular sealing members 19, 20, and suction is applied to the chamber through pipe 21 to remove any water from the outside of the tube.

The cooled tube then passes through the pair of nip rolls 3 which control the speed at which the tube is travelling, and through banks of infra-red heaters 22 and 23 which raise the temperature of the tube to that required for stretching. The tube is then stretched in the direction transverse to its direction of extrusion by gas under pressure introduced through pipe 24 to inflate the tube, and is simultaneously stretched longitudinally by a pair of nip rolls 25 which collapse, and form an air-tight seal across, the inflated tube, and withdraw the collapsed tube at a rate greater than that at which the extruded tube is withdrawn from the extrusion die by the nip rolls 3.

The "helix" defect, which tends to appear as the rate of film production is increased, can be eliminated by progressively increasing the dynamic viscosity of the aqueous sheath medium, by adding an appropriate thickening agent to the medium supplied via pipe 5 to

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channel 6.

The invention is further illustrated by reference to the following Examples in which biaxially oriented polypropylene film was produced using an apparatus of the kind illustrated in the drawing accompanying the provisional specification save that the external water bath 14 was not employed.

Example 1

This is a comparative Example not according to the invention.

Polypropylene was extruded at a rate of 420 lbs/hour (190.5 kg/hour) through an annular extrusion die having a diameter of 6.5 inches (165 mm) and a die gap of 0.060 inch (1.52 mm). The upstream end of the mandrel was 1 inch (25.4 mm) below the extrusion die, and the mandrel, which had a matt surface, was tapered over its length of 48 inches (1219 mm) from 6.25 inches (158.7 mm) at its upstream end to 6.125 inches (155.6 mm) at its downstream end.

Cooling water, having a viscosity of 1 cP at 20°C, was cooled to 12°C and supplied through pipe 5 at a rate of 36 gallons/hour (163.6 litres/hour) so that an annular sheath 8 of water was formed between the mandrel and tubular extrudate. Water from this sheath accummulated in space 9 and was removed through pipe 12. Cooling water was also circulated through the interior of the mandrel.

The tubular extrudate was drawn down over the mandrel by nip rolls 3 which collapsed the tube over only part of its width, and which rotated at a peripheral speed of 15 feet/minute (4.57 m/minute). The tube was then heated to a temperature of about 160°C by infra-red heaters 22 and 23, and inflated to form a bubble of diameter 46.5 inches (1181 mm) by air introduced through pipe 24 at a pressure of 5 inches water gauge (12.7×10^{-3} kgf/cm^2). The tube was also stretched in the longitudinal direction of extrusion by nip rolls 25 rotating at a peripheral speed of 120 feet/minute (36.6 m/minute).

The tubular extrudate exhibited a helical corrugation defect on its surface, and, in consequence of the irregular cooling effect achieved by the water sheath, drawing of the film occurred non-uniformly. The bubble neck oscillated wildly, and could not be controlled in a stable position.

Examples 2 to 4

The procedure of Example 1 was repeated except that the normal cooling water fed to the annular sheath was replaced by an aqueous solution containing sufficient amounts of 'Polycell' ('Polycell' is a registered Trade Mark) wallpaper paste to provide solutions having dynamic viscosities at 20°C as follows:

Example	*Viscosity cP*
2	2
3	9
4	42

A significant reduction in "helix" formation, and improvement in bubble stability, compared to Example 1, was achieved by increasing the viscosity of the cooling solution to 2 cP (Example 2), and the defect was virtually eliminated by further increasing the viscosity to 9 cP (Example 3). No trace of the "helix" defect or of bubble instability was observed on prolonged operation of the system with a cooling solution having a viscosity of 42 cP (Example 4).

WHAT WE CLAIM IS:-

1. A method of cooling an extruded tube of plastics material comprising feeding the tube from an extrusion die, in heat-transfer relationship with an adjacent cooling surface, maintaining said cooling surface at a temperature below the melting point of the plastics material, maintaining between, and in contact with, the tube and said cooling surface, a continuous sheath of a heat-transfer liquid having a dynamic viscosity at 20°C of from 2 to 20,000 centipoise, and withdrawing the cooled tube from said surface.

2. A method according to claim 1 including the further steps of reheating the cooled tube to its orienting temperature, transversely expanding the reheated tube by the introduction therein of a pressurising gas, and longitudinally extending the expanded tube to form a biaxially oriented tubular film.

3. A method according to either of claims 1 to 2 wherein the heat-transfer liquid has a boiling point less than the temperature of the die during extrusion of the tube.

4. A method according to any one of the preceding claims wherein the heat-transfer liquid is an aqueous solution or dispersion of a viscosity modifier.

5. A method according to claim 4 wherein the viscosity modifier is a cellulosic resin.

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6. A method according to any one of the preceding claims wherein the heat-transfer liquid is supplied to the sheath at a rate of from 0.02 to 0.5 litres/minute/centimetre width of tube surface.

7. A method according to any one of the preceding claims wherein the dynamic viscosity of the heat-transfer liquid at 20°C is from 10 to 10,000 centipoise.

8. A method according to any one of the preceding claims wherein the cooling surface comprises an internal mandrel extending axially within the extruded tube.

9. A method according to any one of the preceding claims wherein the tube is a coextruded multiple-layer structure.

10. A method according to any one of the preceding claims wherein the plastics material is a substantially crystalline polymer of propylene.

11. A method substantially as herein described and with reference to any one of Examples 2 to 4.

12. A method substantially as herein described and with reference to the drawing.

13. A cooled plastics tube produced by the method of any one of the preceding claims.

14. A biaxially oriented film produced by the method of any one of claims 2 to 12.

J L RHIND
Agent for the Applicants

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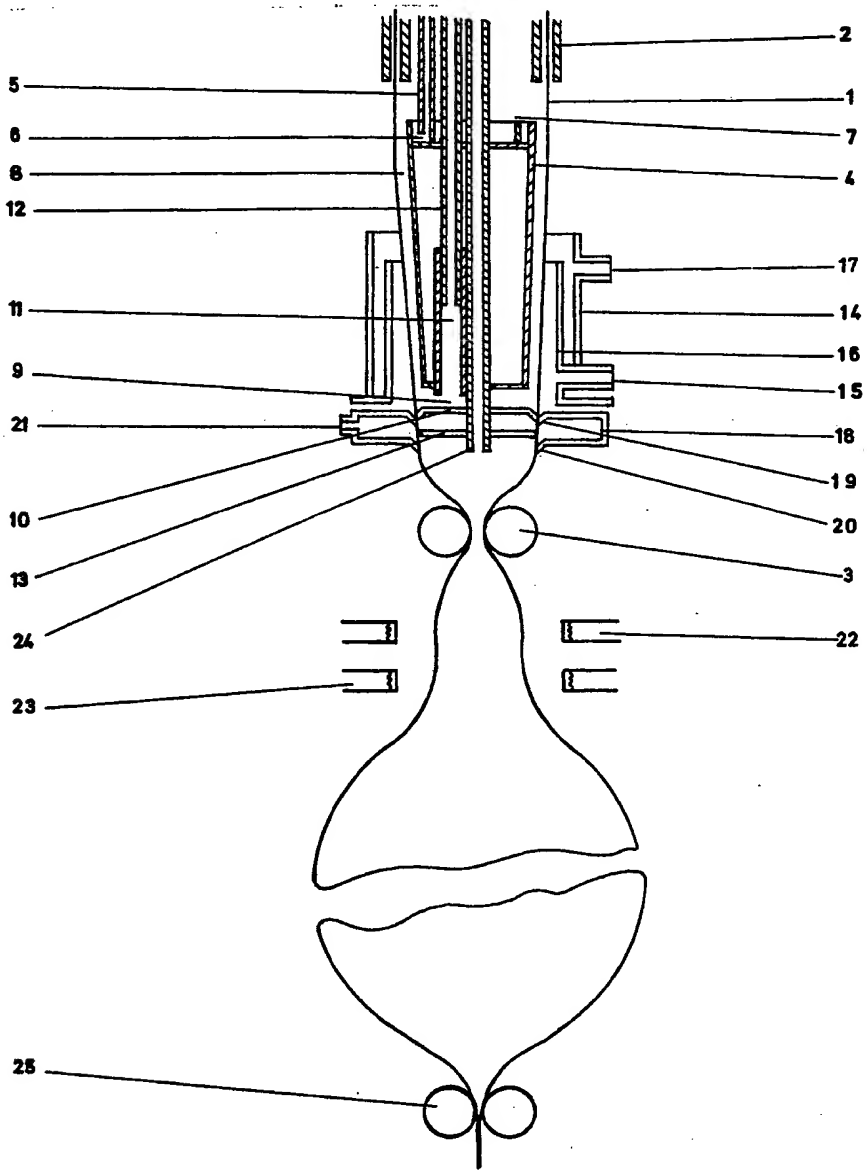
1560550 PROVISIONAL SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*



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